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LETTER

Spontaneous formation of the B2 phase from a decagonal quasicrystal under reduced constraint

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Since the discovery that vacancies can quasiperiodically order in a basic B2 structure to yield a one-dimensional quasiperiodicity, these phases were subjected to intense investigations for possible links with quasicrystal [1, 2]. The B2 phase was found to coexist extensively with the icosahedral quasicrystalline phase, particularly in Al–Cu–TM (TM = transition metal) systems where the two phase fields are often adjacent to each other [3]. The two phase exhibit a well-defined orientation relationship. There exist several studies dealing with quasicrystalline to B2 transformation, particularly in decagonal quasicrystals Döblinger et al. [4] has carefully explored different metastable states in Al–Co–Ni decagonal quasicrystals including nanodomained 1D quasicrystals and multiple twinned approximant phase. The decagonal to a cubic B2 ordered phase transformation can often be observed. The nanocrystals of the B2 phase could be observed on the surface of the decagonal quasicrystal. Zhang and Urban [5] have studied the stability of the QC phase by employing electron irradiation in an electron microscope and observed the transformation of the decagonal quasicrystal (DQC) phase, in an Al–Cu–Co–Si alloy, first to a disordered phase [body centered cubic (BCC phase)] and then to an ordered B2 phase. Zurkirch et al. [6] observed a decagonal to crystalline structural transformation occurring on a surface of Al–Co–Ni upon sputtering the surface. The annealing treatment was found to restores the decagonal structure. Shimoda et al. [7] confirmed the above observation. A similar result has been reported recently by Fluckinger et al. [8] who have reported more than one variant of the cubic crystal at the surface. These authors attributed the structural change to the change in the surface composition during sputtering. The annealing treatment allows the Al atoms from the subsurface to diffuse back and restore the composition resulting in a reappearance of the decagonal quasicrystal. The formation of a BCC phase during ion milling has also been reported in Al–Cu–Co decagonal quasicrystals [9]. Recently Muthy et al. [10] has reported a quasicrystalline to β phase transformation in as-cast $Al_{65}Cu_{20}Fe_{15}$, $Al_{65}Cu_{20}Co_{15}$ and $Al_{72}Pd_{19.5}Mn_{8.5}$ alloys during high energy ball milling. They have correlated the phase change with a critical grain size of 20 nm.

Dong et al. have carried out extensive investigations on the occurrence of B2 phase. This resulted in the realization that the valence electron concentration of

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the B2 phase is similar to that of a quasicrystal [2]. The B2 phase, therefore, exhibited many of the special properties normally associated with the quasicrystal. It was also shown that the B2 phase can be considered as an approximant phase of the icosahedral quasicrystal by going through a two stage process of obtaining approximant hyper crystal followed by the projection in the physical space [11]. Recently Steurer has proposed that a projection from a five dimensional modulated lattice can lead to a defected B2 phase with average atoms which can explain the observed decagonal to B2 transformation [12]. In the present paper, we will explore the close relationship between the decagonal quasicrystal and B2 phase. In particular we will report a spontaneous transformation of ordered decagonal phase to B2 phase at room temperature in the thin foil, which was apparently mediated by the relaxation process at the thin edges of the sample.

The $Al_{64}Cu_{20}Fe_{11}Co_5$ alloy and $Al_{70}Ni_{13}Co_{13}Si_4$ alloy was manufactured in Ar atmosphere by a conventional melting and casting technique [13]. The single quasicrystals of $Al_{70}Ni_{15}Co_{15}$ were grown under Ar atmosphere by the Czochralski method from the melt of composition, $Al_{75}Ni_{145}Co_{105}$ [14]. High resolution electron micrographs (HREM) and electron diffraction patterns of the single quasicrystal were taken with JEM 4000EX, JEM 3000F and Philips CM20. The transmission electron microscope (TEM) specimen of the as-cast $Al_{70}Ni_{13}Co_{13}Si_4$ alloy was prepared by ion milling of the sliced crystal, while those of the $Al_{70}Ni_{15}Co_{15}$ single crystal and as-cast $Al_{64}Cu_{20}Fe_{11}Co_5$ alloy were prepared by dispersing the crushed crystals on the Cu grid with perforated carbon films.

Figure 1a shows the microstructure of $Al_{64}Cu_{20}Fe_{11}Co_5$ alloy in the as-cast condition. In this

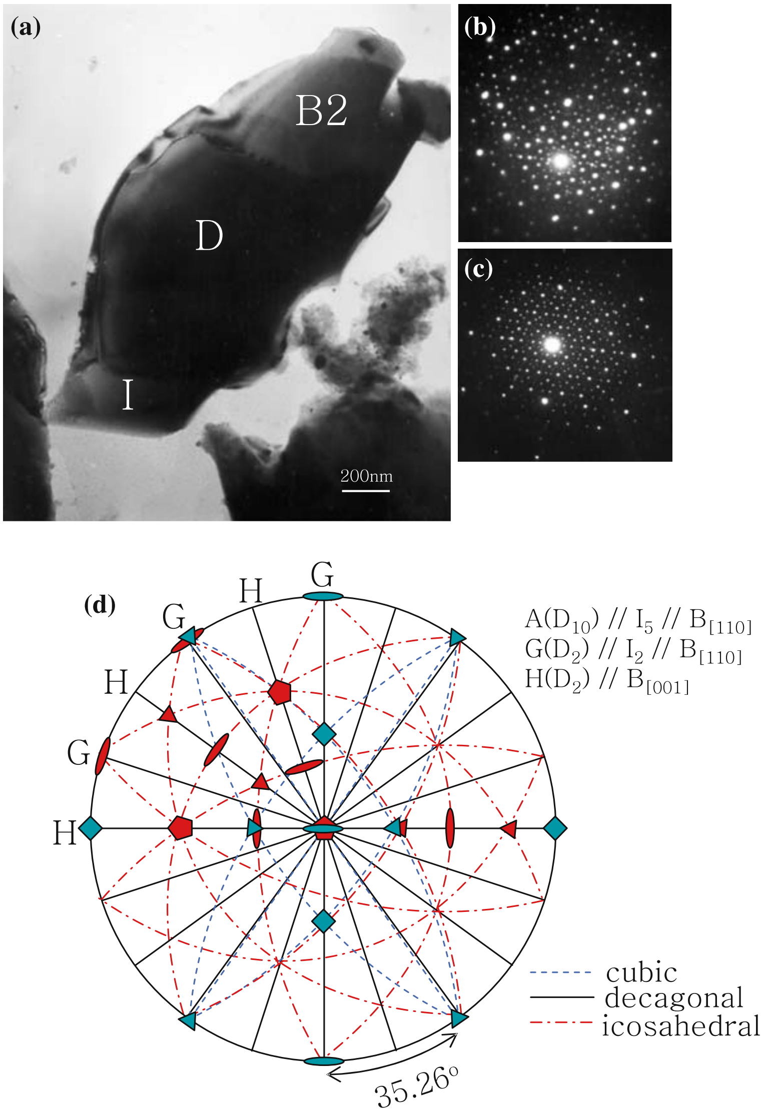

Fig. 1 Transmission electron micrographs of conventionally cast $Al_{64}Cu_{20}Fe_{11}Co_5$ alloy showing the coexistence of icosahedral, decagonal and B2 phases. Bright field image (**a**), and composite electron diffraction patterns of decagonal 10-fold and B2 [110] (**b**) and icosahedral 5-fold and decagonal 10-fold (**c**) zone axes, respectively. The stereogram showing orientation relationship among cubic, decagonal and icosahedral structures (**d**). Some symmetry symbols are omitted for simplicity

composition, the icosahedral and decagonal phase coexisted along with the B2 phase, enabling us to establish an orientation relationship among the three phases (Fig. 1b, c). The orientation relationship is given by;

$$[I5]//[D10]//[110]_{B2}$$
$$[D2]//[001]_{B2}$$

The stereogram showing this orientation relationship is given in Fig. 1d. The B2 phase in this alloy is well distributed. One can observe several B2 grains coexisting with icosahedral and decagonal grains in the interior portions of the specimen. In contrast, in $Al_{70}Ni_{13}Co_{13}Si_4$ alloys containing predominantly decagonal phase, a band of crystalline phase can be observed at the edge of the thin foil (Fig. 2a). Figure 2b shows a micro diffraction pattern obtained from one of the crystal, and clearly identifies the cubic structure. Figure 2c shows a composite diffraction pattern taken from a region comprising of a crystalline grain and a decagonal grain oriented along the 10-fold axis. The ordered spots of B2 phase (marked by the arrow) can be clearly seen. This gives the same orientation relationship previously reported between the decagonal and B2 phases (Fig. 1d). There exists a body of work reporting the transformation of the icosahedral and decagonal phases to the B2 phase [2–12, 15–17]. Often this transformation is attributed to a change in concentration during thinning by ion bombardment and the resultant loss of aluminium atoms, and to the consequent shift of the alloy composition to the adjacent B2 phase field. In order to eliminate the effect of composition change, we have designed the following experiments.

We started with a Czochralski grown single crystal of $Al_{70}Ni_{15}Co_{15}$ with high perfection and composition homogeneity [18]. A portion of this single crystal was crushed to obtain a single quasicrystalline flake with an electron transparent thin edge. The sample was directly observed in a high resolution transmission electron microscope without any further preparation to prevent change in composition during specimen preparation. Figure 3 shows a typical HREM The B2 crystalline phase can be seen at the thin edges. The extent of the phase, however, was smaller than the ion milled case. The sizes of the individual B2 grains were approximately 5 nm. The (110) lattice fringes can be clearly observed in each grain with a spacing of ~0.205 nm. The HREM also established only five orientations of the (110) fringes aligned across 10-fold rotation axis of

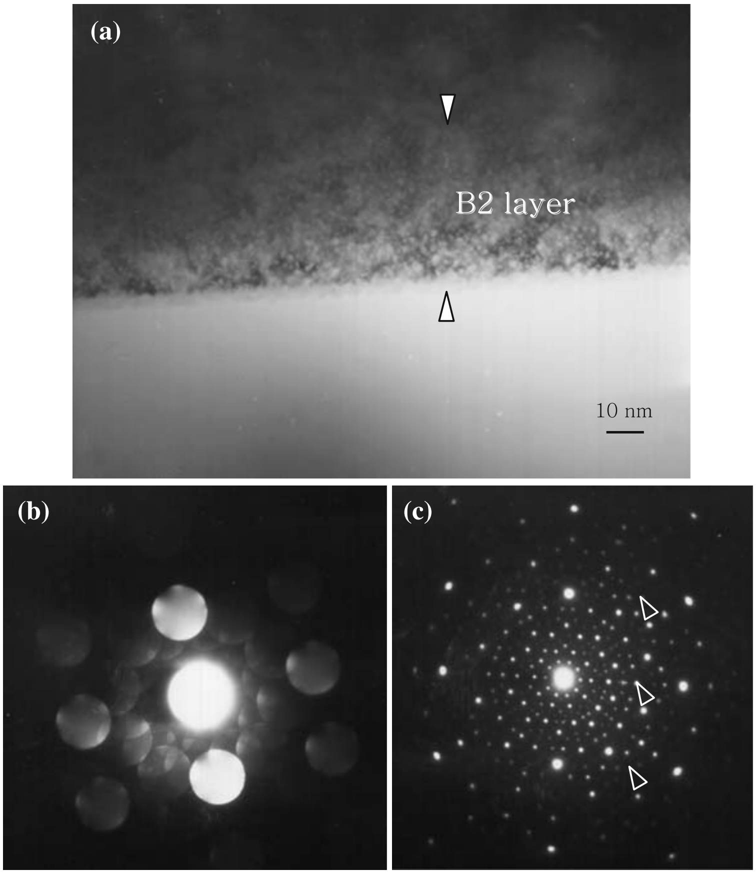

Fig. 2 Transmission electron micrographs of conventionally cast $Al_{70}Ni_{13}Co_{13}Si_4$ showing the formation of B2 phase at the thin edges of the sample. Bright field image (**a**), microdiffraction pattern from the [110] axis of B2 phase (**b**) and composite selected area diffraction pattern of decagonal 10-fold and B2 [110] zone axes (**c**). The ordered spots of B2 phase can be clearly seen (marked by the arrows)

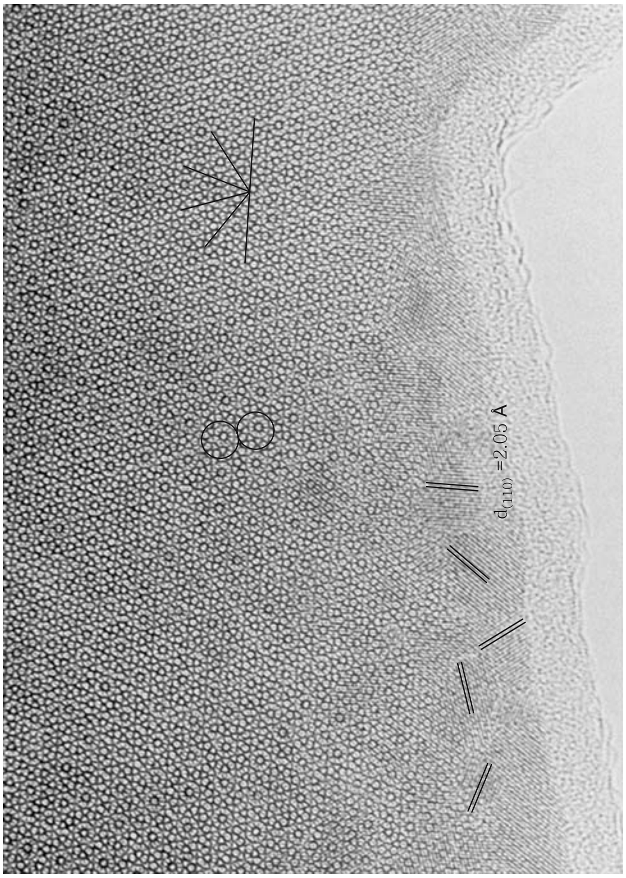

Fig. 3 The high resolution electron micrograph taken from the 10-fold zone axis of decagonal $Al_{75}Ni_{15}Co_{15}$ single crystal. The crystalline B2 phase with ~5 nm sized grains can be seen at the thin edges. Five twin-related variants of the (110) lattice fringes with a spacing of ~0.205 nm are clear. Typical decagon clusters with 2 nm diameters are encircled

the decagonal phase. This indicates that the B2 grains have a fiber texture along the 10-fold axis of the decagonal phase.

In order to measure the composition changes at the thin edge, we employed energy dispersive X-ray spectroscopy (EDS) analysis using field emission TEM (JEM 3000F) equipped with Oxford Inca EDS system. The beam is moved in 7 nm steps. In order to get a reliable result, we have moved the beam both from the edge to the interior and from interior to the B2 phase. The amorphous layer at the edge primarily consists of ‘C’ contaminant. For ternary compositions containing both heavy and light elements, quantitative estimates are often difficult. However, since we know the precise composition of our single crystal, it is possible to estimate the deviation from the bulk composition as the probe is moved from the quasicrystal towards the thin edge. Table 1 gives the measured deviations in atomic percentage. As one can see, the composition of B2 phase has not deviated significantly from the quasicrystals composition. The phase field of Al–Co–Ni decagonal phase has recently been evaluated and these deviations lie within the wide phase field of the decagonal phase [19].

Table 1 Deviation of composition (at%) from bulk quasicrystals composition (Al_{70} $Co_{15}Ni_{15}$) near the edge

	B2	Boundary	QC*	QC	QC*	B2
Al	+19	–17	–13	0	–11	09
Co	–01	0	05	0	–03	–03
Ni	–18	+16	+17	0	+14	–14

Measurements are done with beam moved from the edge (left hand of the table) to the center and from center to the edge

*Near boundary

The results presented above show that at the thin edges, the decagonal phase transforms spontaneously to the B2 phase. We first argue that this effect is not related to any composition change. In this sense, our result is unlike some of the earlier reports of quasicrystal-to-B2 transformation [15–17]. The most definitive of such work is that of Zurkirch et al. [6], who have shown that 15 KeV Ar^+ ion sputtering leads to the formation of a body centered cubic (BCC) phase. The XPS measurement shows a strong depletion of aluminium at the surface. This change in composition leads to the stabilization of a BCC based ordered structure. Thus, argon ion milling of our specimen may have contributed to the occurrence of the B2 phase in our as-cast Al–Ni–Co–Si alloy (Fig. 2). The most significant observation of Zurkirch et al. [6], however, is that the decagonal phase is recovered when the sample is annealed at 700 K. This structural change, coupled with composition analysis, clearly establishes that aluminium tends to segregate at the surface of the Al–Co–Ni decagonal quasicrystalline phase. Our observations of the B2 phase near the thin edges of the flake sample obtained from a large unidirectional grown single quasicrystal without resorting to ion milling or chemical thinning procedure cannot be rationalized by invoking the argument of composition change and in particular aluminium depletion put forward in some of the earlier work. We, therefore, conclude that the ordered decagonal phase we observed spontaneously transformed to the B2 phase at the thin edges. We further note that the temperature of our specimen, which was prepared from a bulk single crystal, at no stage exceeded the room temperature.

Spontaneous phase transformation at the thin edges of the TEM specimen is well documented in the B2 ordered alloys undergoing shear induced martensite transformation [19–20]. The relaxation of the geometrical constraints at the thin edges leads to spontaneous phonon softening. This, in turn, leads to a structural transformation involving co-operative movements of atoms. A similar situation involving a local shuffle of atoms can be a distinct possibility in the present case. However, if one considers the size of the crystalline domain, a classical diffusional transformation may also be feasible. In general, the diffusivities in the β related structures are among the highest in any metallic system. We assume a parabolic growth law. If the room temperature diffusivity is of the order of 10^{-20} m/s (as is generally observed in the B2 based alloys like β brass) the time needed to grow a 5 nm domain at room temperature will be less than 30 min. This is less than the time that we spent preparing the sample from a single crystal and transferring it to the electron microscope stage. We would also like to point out the possibility of significant surface diffusion, which would enhance the transformation. Thus, a diffusional transformation can account for the phase change. As will be shown later, it is likely that transformation kinetics may not need a long-range transport of atoms. In such a case, interface-controlled kinetics is more likely. However, for growth of small domains, both will yield a similar time scale.

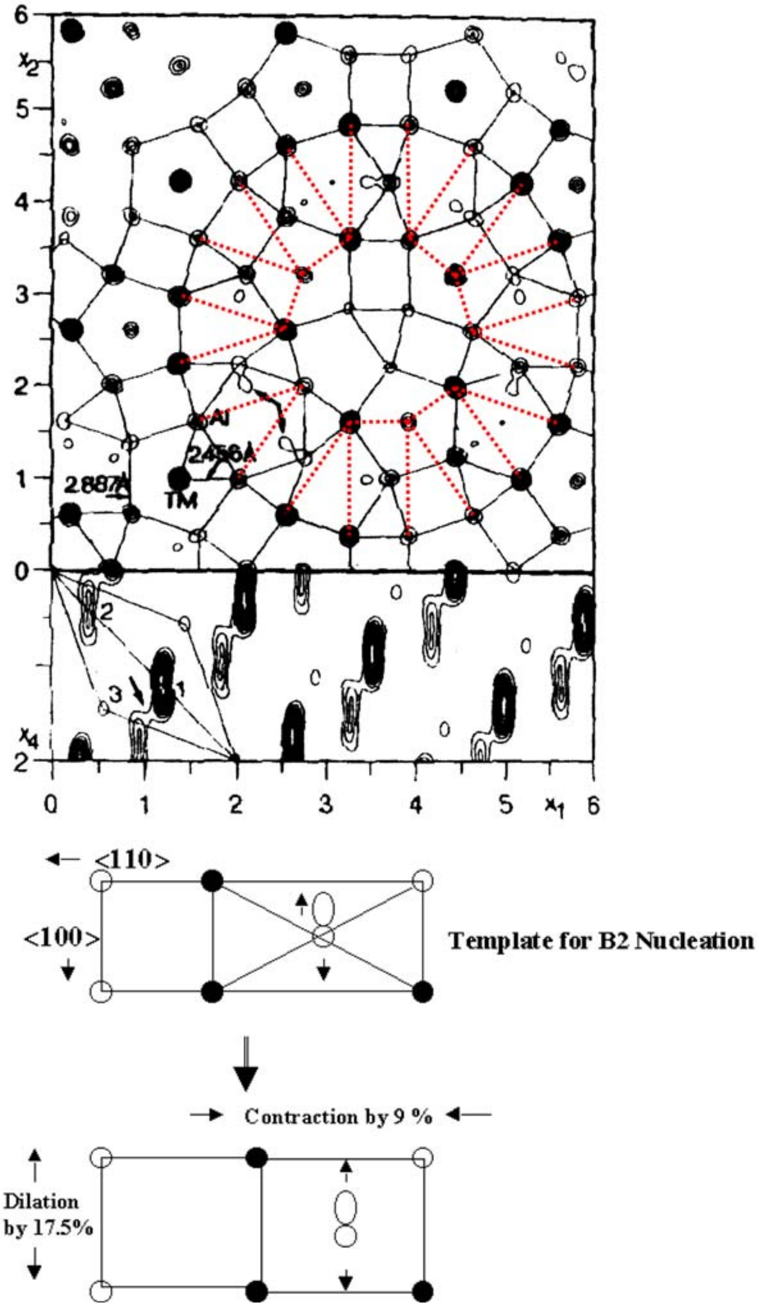

Fig. 4 Electron density map [12] of decagonal $Al_{70}Ni_{15}Co_{15}$ quasicrystal showing the template for B2 nucleation. The B2 lattice can be produced by 9% contraction along the <110> direction and 17.5% dilation along the <100> direction, respectively

Although the nature of ordering is not well understood, the basic structure of the Al–Cu–Co decagonal quasicrystal is well resolved. Figure 4 shows the electron density map of the atomic arrangements in the bottom layer normal to the decagonal axis obtained by Steurer [12]. The structure can be seen to contain remnants of the atomic arrangements of the (110) plane of B2 structure arranged in five twin-related variants (dotted line). As shown in Fig. 4, the (110) plane lattice of B2 phase can be produced from a decagonal structure by 9% contraction along the < 110> direction and 175% dilation along the < 100> direction, respectively. It should also be noted that the interplanar spacing of (110) planes (~0205 nm) is well matched with the periodicity of 041 nm [6] along the 10-fold axis of decagonal phase. Although long-range lattice matching is not possible due to the quasiperiodicity of decagonal 10-fold plane, local lattice match between the B2 and decagonal phases can reduce the interfacial energy and assist the nucleation of B2 phase from the decagonal phase. A similar conclusion was arrived at by Zurkirch et al. [6] who examined the tiling model of Burkov [21] for decagonal layer. This model closely resembles experimental findings of Steurer et al. [22]. The concept of chemical twinning of basic CsCl structure has been proposed recently by Dong et al. [23] to explain the origin of icosahedral clusters in the quasicrystals and related approximants. It is attractive to propose a spontaneous chemical detwinning process at lower dimensional state to account for the decagonal-to-B2 transformation. However, requirement of significant local rearrangements suggests that such a process is more likely associated with a diffusional process rather than a coordinated shear transformation that has been observed earlier at the thin edges of B2 CuZn samples.

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References

1. Chattopadhyay K, Lele S, Thangaraj N, Ranganathan S (1987) Acta Metall 35:727
2. Dong C (1995) Scripta Metall Mater 33:239
3. Dong C, Perrot A, Dubois JM, Belin E (1994) Mater Sci Forum 403:150
4. Döblinger M, Wittmann R, Grushko B (2001) Phys Rev B 64:134208
5. Zhang H, Urban K (1992) Phil Mag Lett 209:66
6. Zurkirch M, Bolliger B, Erbudak M, Kortan AR (1998) Phys Rev B58:14113
7. Shimoda M, Guo JQ, Sato TJ, Tsai A-P (2000) Surf Sci 454–456:11
8. Flückiger T, Michlmayr T, Biely C, Lüscher R, Erbudak M (2003) Appl Surf Sci 212–213:43
9. Mukhopadhyay NK, Weatherly GC (2001) Mater Sci Eng A 304–306:855
10. Murty BS et al (2004) J Non Cryst Solids 334&335:48
11. Dong C, Wang DH, Wang YM, Ge F, He FZ, Zhang QH, Chattopadhyay K, Ranganathan S (1998) In: Proc of 6th International Conference on Quasicrystals. 223
12. Stuerer W (2000) Mater Sci Eng 294–296:268
13. Song GS, Kim WT, Kim DH, Zhong ZZ, Yang GC, Zhou YH (2000) J Mater Sci Lett 19:363
14. Jeong HT, Kim SH, Kim WT, Kim DH, Inkson BJ (2000) J Cryst Growth 217:217
15. Chien CL, Lu M (1992) Phys Rev B45:12793
16. Beeli C, Horiuchi S (1994) Phil Mag B70:215
17. Dong C, Dubois JM, Kang SS, Audier M (1992) Phil Mag B65:107
18. Yushenko M, Grushko B, Velikanova TA, Urban K (2004) J Alloy Compound 367:20
19. Hull D (1962) Phil Mag 7:537
20. Chattopadhyay K (1985) Z Metallkde 76:496
21. Burkov SE (1991) Phys Rev Lett 67:614
22. Steurer W, Haibach T, Zhang B, Kek S, Luck R (1993) Acta Crystallogr B49:661
23. Dong C, Zhang Q, Wang D, Wang Y (1999) Philos Mag A 79:501